Electronic Supporting Information

Influence of Aromatic Structure on the Thermal Behaviour of Lignin

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Supporting Table S1

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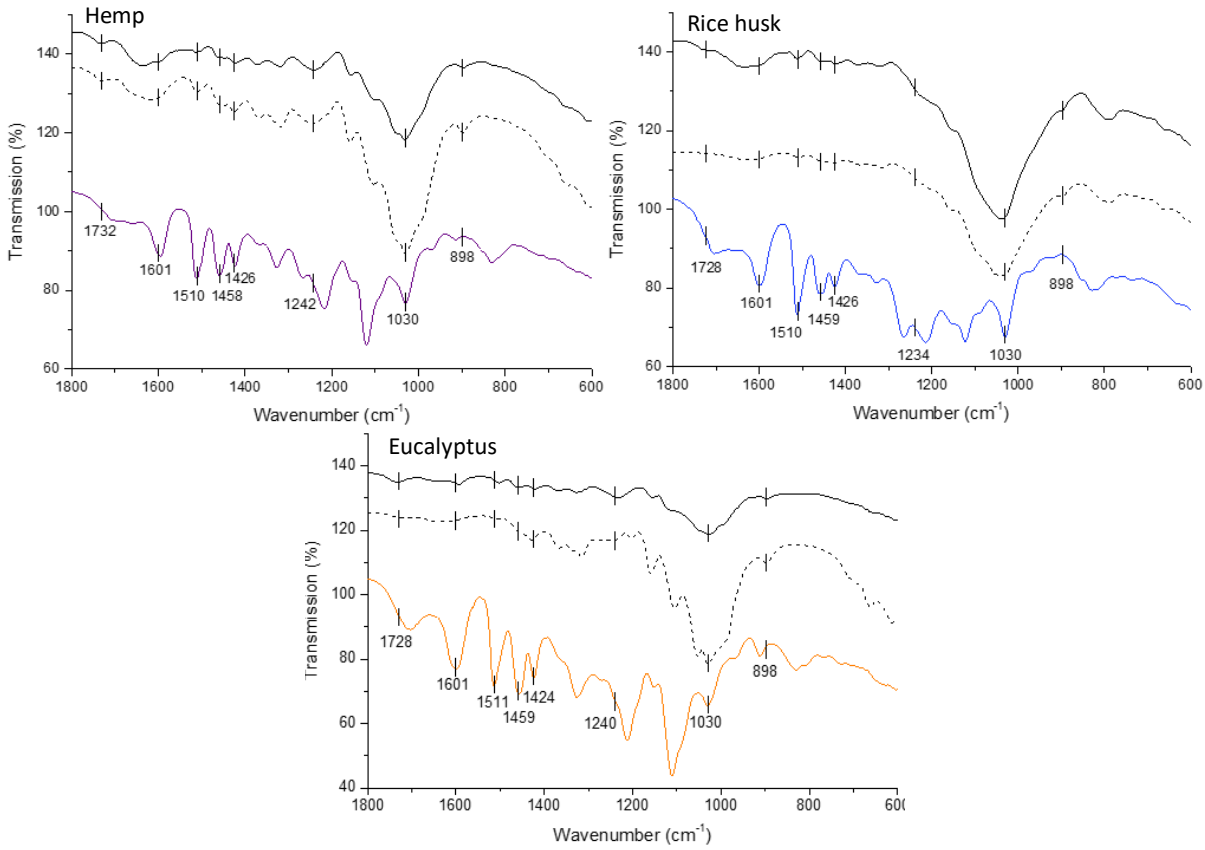

Figure S1- FTIR spectra of (——) ground biomass (hemp herds, rice husk or eucalyptus chips), the resulting (– –)pulp, and (coloured line) lignin following organosolv extraction. Spectra were recorded from 4000 to 600 cm^{-1}, over 32 scans with a resolution of 4 cm^{-1}. Spectra have been offset along the transmission axis, and the region between 1800 and 600 cm^{-1} has been focused on for clarity. Full spectra of flax and other biomass investigated is included in the supplementary information.

Table S1- Assignment of main lignin 13 C 1 H cross-peaks in the HSQC spectra shown in Figure 3 and 4.

Label	Typical peak (δ_C/δ_H)	Lignin type				Assignment
		Rice husk	Flax	Hemp	Eucalyptus	
B_β	53.6/3.45	53.9/3.46	53.8/3.47	53.9/3.48	53.6/3.49	C_β-H_β in phenylcoumaran substructures
C_β	54.2/3.05	54.3/3.06	54.2/3.07	54.2/3.06	54.3/3.07	C_β-H_β in resinol substructures
OCH_3	56.3/3.75	56.1/3.76	56.1/3.76	56.3/3.75	56.3/3.75	C-H in methoxyls
A_γ	60.3/3.63	60.3/3.60	60.4/3.60	60.4/6.63	60.4/3.65	β-O-4 substructures
I_γ	61.1/4.05	60.4/4.05	60.3/4.04	60.4/4.05	60.3/4.05	C_γ–H_γ in p-hydroxycinnamyl alcohol end groups
A' & A''	63.8/3.83-4.30	n/a	n/a	n/a	n/a	C_γ–H_γ in γ–acylated β-O-4' substructures
C_γ	63.6/3.63	63.3/3.71	63.3/3.71	63.3/3.71	63.3/3.72	C_γ–H_γ in phenylcoumarane substructures
B_γ	71.3/3.77 & 4.09	71.3/3.75 & 4.05	71.3/3.75 & 4.05	71.7/3.80 & 4.05	71.7/3.80 & 4.06	C_γ–H_γ in resinol substructures
A_β	80.4/4.5. 84.4/4.4 & 85.6	84.2/4.31	84.2/4.31 & 86.4/4.12	84.3/4.32 & 86.5/4.13	84.1/4.32 & 86.5/4.13	C_β-H_β in β-O-4' substructures (A)
A_α	71.9/4.80	71.7/4.76	71.7/4.77	71.8/4.77	72.6/4.89	C_α-H_α in β-O-4' substructures (A) and γ-acetylated β-O-4' substructures (A' & A'')
D_α	82.1/5.12	n/a	n/a	n/a	77.8/5.12	C_α-H_α in spirodienone substrctures
Aβ (G)	84.1/4.29	84.2/4.31	84.2/4.31	84.3/4.32	84.1/4.32	acylated β-O-4 substructures
B_α	85.6/4.62	85.5/4.62	85.6/4.64	85.7/4.64	85.8/4.64	C_α-H_α in resinol substructures
A_β (S)	86.5/4.11	n/a	86.4/4.12	86.5/4.13	86.5/4.13	C_β-H_β in β-O-4' substructures (A)
C_α	87.0/5.43	87.6/5.45	87.6/5.45	87.6/5.45	87.6/5.44	C_α-H_α in phenylcoumarane substructures
$S_{2,6}$	104.2/6.63	104.1/6.66	104.1/6.66	104.1/6.66	104.1/6.63	$C_{2,6}$ - $H_{2,6}$ in syringyl unit
$S'_{2,6}$	106.7/7.36 & 7.21	104.7/7.35	n/a	106.8/7.33	106.8/7.33	$C_{2,6}$ - $H_{2,6}$ in oxidised (C_α=O) syringyl unit
G_2	110.5/6.90	110.8/6.93	110.8/6.93	110.9/6.93	111.0/6.93	C_2-H_2 in guaiacyl unit
FA_2	111.8/7.34	111.7/7.33	112.4/7.33	n/a	110.7/7.48	Ferulic acid
G_5	115.2/6.71 & 6.94	115.7/6.77 & 6.93	115.7/6.76 & 6.94	115.7/6.78 & 6.95	115.8/6.76 & 6.95	C_5-H_5 in guaiacyl unit
G_6	119.5/6.83	119.1/6.77	119.1/6.78	119.3/6.77	119.4/6.78	C_6-H_6 in guaiacyl unit
FA_6	123.1/7.1	121.6/7.06	n/a	n/a	n/a	Ferulic acid
J_β	126.4/6.94	126.2/6.96	126.1/6.97	126.2/6.96	126.7/7.01	Cinnamaldehyde end group
$H_{2,6}$	128.1/7.27	128.3/7.24	n/a	128.3/7.24	n/a	$C_{2,6}$ - $H_{2,6}$ in *p*-hydroxyphenyl units
I_α	130.6/6.3	130.7/6.32	130.8/6.32	130.8/6.33	130.9/6.32	C_α–H_α in cinnamyl alcohol end-groups
$PCA_{2,6}$	130.7/7.48	130.6/7.47	n/a	130.7/7.51	n/a	$C_{2,6}$-$H_{2,6}$ in *p*-coumaric acid

Figure S2- Images of industrial organosolv lignin derived chars carbonised from room temperature to (A) 350 °C and (B) 900 °C, at 5 °C/min, held at temperature for 30 minutes, under a flow of argon (500 ml/min)

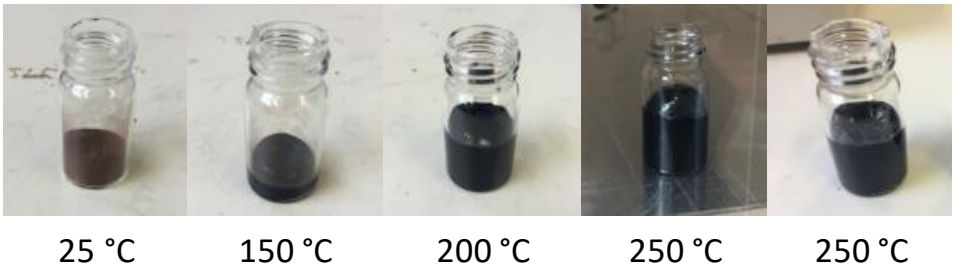

Figure S3- Images of industrial organosolv lignin samples heat in a conventional oven to the temperatures listed. By 150 °C lignin had formed a melt. Expansion of the sample onset between 150 and 200 °C, and continued to the maximum temperature investigated of 250 °C. On removal from oven the 250 °C char deflated.

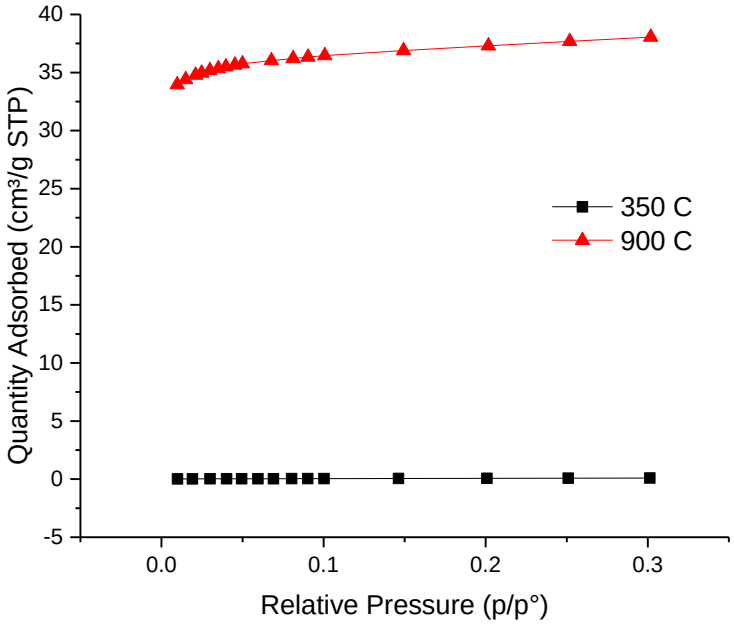

Figure S4- Nitrogen sorption isotherm for char carbonised under argon from industrial organosolv lignin at 900 °C for 30 mins.